

<b>METHOD #:</b> 410.1	Approved for NPDES (Editorial Revision 1978)
<b>TITLE:</b>	Chemical Oxygen Demand (Titrimetric, Mid-Level)
<b>ANALYTE:</b>	COD Chemical Oxygen Demand
<b>INSTRUMENTATION:</b>	N/A
<b>STORET No.</b>	00340

## 1.0 Scope and Application

- 1.1 The Chemical Oxygen Demand (COD) method determines the quantity of oxygen required to oxidize the organic matter in a waste sample, under specific conditions of oxidizing agent, temperature, and time.
- 1.2 Since the test utilizes a specific chemical oxidation the result has no definite relationship to the Biochemical Oxygen Demand (BOD) of the waste or to the Total Organic Carbon (TOC) level. The test result should be considered as an independent measurement of organic matter in the sample, rather than as a substitute for the BOD or TOC test.
- 1.3 The method can be applied to domestic and industrial waste samples having an organic carbon concentration greater than 50 mg/L. For lower concentrations of carbon such as in surface water samples, the Low Level Modification should be used. When the chloride concentration of the sample exceeds 2000 mg/L, the modification for saline waters is required.

## 2.0 Summary of Method

- 2.1 Organic and oxidizable inorganic substances in the sample are oxidized by potassium dichromate in 50% sulfuric acid solution at reflux temperature. Silver sulfate is used as a catalyst and mercuric sulfate is added to remove chloride interference. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as an indicator.

## 3.0 Sampling and Preservation

- 3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.
- 3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.
- 3.3 Samples should be preserved with sulfuric acid to a pH < 2 and maintained at 4°C until analysis.

## 4.0 Interferences

- 4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.
  - 4.1.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.
  - 4.1.2 Glassware used in the test should be conditioned by running blank procedures to eliminate traces of organic material.
- 4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step. To minimize this loss the flask should be cooled during addition of the sulfuric acid solution.
- 4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine and estuarine samples.

## 5.0 Apparatus

- 5.1 Reflux apparatus: Glassware should consist of a 500 mL Erlenmeyer flask or a 300 mL round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint. Any equivalent reflex apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

## 6.0 Reagents

- 6.1 Distilled water: Special precautions should be taken to insure that distilled water used in this test be low in organic matter.
- 6.2 Standard potassium dichromate solution (0.250 N): Dissolve 12.259 g  $K_2Cr_2O_7$ , primary standard grade, previously dried at 103°C for two hours, in distilled water and dilute to 1000 mL.
- 6.3 Sulfuric acid reagent: Conc.  $H_2SO_4$  containing 23.5 g silver sulfate,  $Ag_2SO_4$ , per 4.09 kg bottle. With continuous stirring, the silver sulfate may be dissolved in about 30 minutes.
- 6.4 Standard ferrous ammonium sulfate (0.25 N): Dissolve 98.0 g of  $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$  in distilled water. Add 20 mL of conc.  $H_2SO_4$  (6.8), cool and dilute to 1 liter. This solution must be standardized daily against standard  $K_2Cr_2O_7$  solution (6.2).
  - 6.4.1 Standardization: To approximately 200 mL of distilled water add 25.0 mL of 0.25 N  $K_2Cr_2O_7$  (6.2) solution. Add 20 mL of  $H_2SO_4$  (6.8) and cool. Titrate with ferrous ammonium sulfate (6.4) using 3 drops of ferroin indicator (6.6). The color change is sharp, going from blue-green to reddish-brown.

$$\text{Normality} = \frac{(\text{mL } K_2Cr_2O_7) (0.25)}{\text{mL } Fe(NH_4)_2 (SO_4)_2}$$

- 6.5 Mercuric sulfate: Powdered  $\text{HgSO}_4$ .
- 6.6 Phenanthroline ferrous sulfate (ferroin) indicator solution: Dissolve 1.48 g of 1-10 (ortho) phenanthroline monohydrate, together with 0.70 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 100 mL of water. This indicator may be purchased already prepared.
- 6.7 Silver sulfate: Powdered  $\text{Ag}_2\text{SO}_4$ .
- 6.8 Sulfuric acid (sp.gr. 1.84): Concentrated  $\text{H}_2\text{SO}_4$ .

## 7.0 Procedure

- 7.1 Place several boiling stones in the reflux flask, followed by 50.0 mL of sample or an aliquot diluted to 50.0 mL and 1 g of  $\text{HgSO}_4$  (6.5). Add 5.0 mL conc.  $\text{H}_2\text{SO}_4$  (6.8); swirl until the mercuric sulfate has dissolved. Place reflux flask in an ice bath and slowly add, with swirling, 25.0 mL of 0.025 N  $\text{K}_2\text{Cr}_2\text{O}_7$  (6.2). Now add 70 mL of sulfuric acid-silver sulfate solution (6.3) to the cooled reflux flask, again using slow addition with swirling motion. Caution: Care must be taken to assure that the contents of the flask are well mixed. If not, superheating may result, and the mixture may be blown out of the open end of the condenser.
  - 7.1.1 If volatile organics are present in the sample, use an allihn condenser and add the sulfuric acid-silver sulfate solution through the condenser, while cooling the flask, to reduce loss by volatilization.
- 7.2 Apply heat to the flask and reflux for 2 hours. For some waste waters, the 2-hour reflux period is not necessary. The time required to give the maximum oxidation for a wastewater of constant or known composition may be determined and a shorter period of refluxing may be permissible.
- 7.3 Allow the flask to cool and wash down the condenser with about 25 mL of distilled water. If a round bottom flask has been used, transfer the mixture to a 500 mL Erlenmeyer flask, washing out the reflux flask 3 or 4 times with distilled water. Dilute the acid solution to about 300 mL with distilled water and allow the solution to cool to about room temperature. Add 8 to 10 drops of ferroin indicator (6.6) to the solution and titrate the excess dichromate with 0.25 N ferrous ammonium sulfate (6.4) solution to the end point. The color change will be sharp, changing from a blue-green to a reddish hue.
- 7.4 Blank-Simultaneously run a blank determination following the details given in (7.1) and (7.2), but using low COD water in place of sample.

## 8.0 Calculation

- 8.1 Calculate the COD in the sample in mg/L as follows:

$$\text{COD, mg/L} = \frac{(A - B)N \times 8,000}{S}$$

where:

- A = milliliters of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution required for titration of the blank,
- B = milliliters of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution required for of the sample,
- N = normality of the  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution, and
- S = milliliters of sample used for the test.

## 9.0 Precision and Accuracy

- 9.1 Eighty-six analysts in fifty-eight laboratories analyzed a distilled water solution containing oxidizable organic material equivalent to 270 mg/L COD. The standard deviation was  $\pm 17.76$  mg/L COD with an accuracy as percent relative error (bias) of -4.7%. (EPA Method Research Study 3).

### **Bibliography**

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 550, Method 508 (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1252-67, p 473 (1976).